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(54) Metallocene catalysts with lewis acids and aluminum alkyls.

(57) This invention is for a catalyst system comprising a neutral metallocene compound, an aluminum alkyl and a Lewis acid. The Lewis acid must be of sufficient acidity to ionize a neutral metallocene compound to form a cationic metallocene catalyst. The ligands of the Lewis acid should not be reactive with the metallocene cation. Any metallocene catalyst compound having two cyclopentadienyl rings attached to a transition metal would be useful in this invention.

The invention is also for the process of using the catalyst system in polymerization of olefins. The metallocene is contacted with the Lewis acid. The aluminum alkyl is contacted with the olefin. The two mixtures are contacted with each other under polymerization conditions.

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METALLOCENE CATALYSTS WITH LEWIS ACIDS AND ALUMINUM ALKYLS

FIELD OF THE INVENTION:

This invention relates, in general, to an improved catalyst system and a process for using the improved catalyst system and, specifically, to a catalyst system of a metallocene compound with a Lewis acid and an aluminum alkyl and a process for using the improved catalyst system for polymerization of olefins, primarily propylene.

10 DESCRIPTION OF RELATED ART:

The use of metallocene compounds as catalysts for the polymerization of olefins is known. German patent application No. 2,608,863 discloses a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl)titanium dialkyl, an aluminum trialkyl and water. German patent application No. 15 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein Y represents $\text{R}_1\text{CH}_2\text{AlR}_2$, $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ where R stands for an alkyl or metallo alkyl, and n is a number within the range 1-4; and the metallocene catalyst is used in combination with an aluminum trialkyl cocatalyst and water.

The use of metallocenes as catalysts in the copolymerization of ethylene and other alpha-olefins is also known in the art. U.S. Pat. No. 4,542,199 to Kaminsky, et al. discloses a process for the polymerization of olefins and particularly for the preparation of polyethylene and copolymers of polyethylene and other alpha-olefins. The disclosed catalyst system includes a catalyst of the formula $(\text{cyclopentadienyl})_2\text{MeRHAl}$ in which R is a halogen, a cyclopentadienyl or a $\text{C}_1\text{-C}_6$ alkyl radical, Me is a transition metal, in particular zirconium, and Hal is a halogen, in particular chlorine. The catalyst system also includes an alumoxane having the general formula $\text{Al}_2\text{OR}_4(\text{Al}(\text{R})\text{-O})_n$ for a linear molecule and/or $(\text{Al}(\text{R})\text{-O})_{n+2}$ for a cyclic molecule in which n is a number from 4-20 and R is a methyl or ethyl radical. A similar catalyst system is disclosed in U.S. Pat. No. 4,404,344.

U.S. Pat. No. 4,530,914 discloses a catalyst system for the polymerization of ethylene to polyethylene having a broad molecular weight distribution and especially a bimodal or multimodal molecular weight distribution. The catalyst system is comprised of at least two different metallocenes and an alumoxane. The patent discloses metallocenes that may have a bridge between two cyclopentadienyl rings with the bridge serving to make those rings stereorigid.

European Patent Publication No. 0185918 discloses a stereorigid, chiral zirconium metallocene catalyst for the polymerization of olefins. The application does not indicate that hafnium could be substituted for the zirconium and used to produce a useful polymer product. The bridge between the cyclopentadienyl groups is disclosed as being a linear hydrocarbon with 1-4 carbon atoms or a cyclical hydrocarbon with 3-6 carbon atoms.

Polymerization of olefins is primarily with Zeigler-Natta catalysts. One family of Zeigler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane (MAO) as a cocatalyst. A system for the production of isotactic polypropylene using a titanium or zirconium metallocene catalyst and an alumoxane cocatalyst is described in "Mechanisms of Stereochemical Control in Propylene Polymerization with Soluble Group 4B Metallocene/Methylalumoxane Catalysts," J. Am. Chem. Soc., Vol. 106, pp. 6355-64, 1984. The article shows that chiral catalysts derived from the racemic enantiomers of ethylene-bridged indenyl derivatives form isotactic polypropylene by the conventional structure predicted by an enantiomorphic-site stereochemical control model. The meso achiral form of the ethylene-bridged titanium indenyl diastereomers and achiral zirconocene derivatives, however, produce polypropylene with a purely atactic structure.

MAO activates the metallocene which then becomes able to promote polymerization of alpha-olefins. Other organometallic compounds of aluminum, such as trimethylaluminum (TMA) or dimethyl aluminum halide, are known not to promote polymerization by themselves. Neither aluminum alkyls nor dimethylaluminum halides alone are active cocatalysts.

A combination of TMA and dimethylaluminum fluoride (DMF) has been shown to be effective as a cocatalyst in place of MAO. DMF is a Lewis acid. Such a combination is reported in "Isotactic Polymerization of Propene: Homogeneous Catalysts Based on Group 4 Metallocenes without Methylalumoxane", A. Zambelli, P. Longo and A. Grassi, Macromolecules, Vol. 22, p. 2186-2189, 1989. The stereochemical

structure of the polymers prepared with TMA/DMF and with MAO were very similar. However, the polymerization yields obtained for TMA/DMF mixtures were substantially lower than those obtained for MAO.

It has also been reported that a metallocene compound with magnesium chloride forms a catalyst system with bis(cyclopentadienyl)thorium dimethyl which is effective to polymerize ethylene. Such a combination is reported in "[$(CH_3)_5C_5$]₂Th(CH₃)₂ Surface Chemistry and Catalysis. Direct NMR Spectroscopic Observation of Surface Alkylation and Ethylene Insertion/Polymerization on MgCl₂". D. Heddin and T. J. Marks, J. Am. Chem. Soc., Vol. 110, No.5, 1988. A methyl group is abstracted from the cyclopentadienyl compound and a cation is formed. The methyl group coordinates with the magnesium to form a magnesium anion. Magnesium chloride is a Lewis acid.

Metallocene catalysts are sensitive to poisons in the absence of a scavenging agent, such as methylaluminoxane. Polymerization requires high concentrations of the cations and frequently end up as either runaway reactions or yield no polymer at all.

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SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a catalyst system of a metallocene compound with a Lewis acid and an aluminum alkyl and a process for using the improved catalyst system for polymerization of olefins. Homopolymers or copolymers produced by the polymerization of alpha olefins may be produced in accordance with the present invention. Propagation of the polymer chain is carried out in the presence of a neutral alkyl derivative of a metallocene compound which has been put into contact with a Lewis acid and an aluminum alkyl. Any metallocene catalyst compound having two cyclopentadienyl rings coordinated to a transition metal would be useful in this invention.

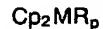
The catalyst is contacted with the Lewis acid. The aluminum alkyl is contacted with the olefin. The two mixtures are contacted with each other under polymerization conditions.

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DESCRIPTION OF THE INVENTION

This invention is for a catalyst system comprising a metallocene catalyst, a Lewis acid and an aluminum alkyl and a process for using the catalyst system for polymerization of olefins.

35 The metallocene catalyst is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, halogen, amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4. M is preferably a Group IV metal such as titanium, zirconium or hafnium and is most preferably zirconium. R is preferably an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms. R is most preferably an alkyl or alkoxy up to six carbons atoms or an aryl up to 10 carbon atoms. The neutral derivative of the metallocene is preferably ethylene bis(tetrahydroindenyl)zirconium dimethyl or ethylene bis(indenyl)zirconium diemthyl and is most preferably ethylene bis(indenyl)zirconium dimethyl.

45 The Lewis acid useful in this invention is any material which can accept an electron pair and is of sufficient acidity to ionize a neutral metallocene to form a cationic metallocene catalyst. In addition, the ligands of the Lewis acid cannot be reactive with the metallocene cation. Preferably, the Lewis acid contains boron or is magnesium chloride (MgCl₂). Most preferably, the Lewis acid is tris(pentafluorophenyl)boron.

The aluminum alkyl is of the general formula AlR₃ where R is halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl. Preferably, the aluminum alkyl is trimethyl aluminum (TMA) or triethyl aluminum (TEAI). Most preferably, the aluminum alkyl is triethyl aluminum.

55 In the practice of this invention, the aluminum alkyl is mixed with the olefin. The Lewis acid is dissolved or slurried in a nonpolar solvent. The neutral metallocene catalyst is dissolved separately in the same solvent. The Lewis acid mixture and the catalyst mixture are combined. The mixture is placed in contact with the blend of olefin and aluminum alkyl. Molar ratios for metallocene:Lewis acid:aluminum alkyl range from 0.01:1:0.1 to 5:1:350 and are preferably from 0.5:1:0.5 to 4:1:25 and are most preferably 0.02:1:1 for Lewis acids which dissolve in a nonpolar solvent and 0.01:1:1 for Lewis acids which form a slurry in

nonpolar solvents.

Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80 °C to 150 °C, preferably 25 °C to 90 °C and most preferably from 50 °C to 80 °C.

The following catalyst system were evaluated with and without addition of an aluminum alkyl and with and without addition of a Lewis acid.

1. iPr(Cp-I-Flu)ZrMe₂/F15/TEAI (TMA)

2. iPr(Cp-I-Flu)ZrMe₂/MgCl₂/TEAI

10 3. Et(Ind)₂ZrMe₂/F-15/TEAI

4. Et(Ind)₂ZrMe₂/MgCl₂/TEAI

Et(Ind)₂ZrMe₂ is ethylenebis(indenyl)zirconium dimethyl, iPr(Cp-I-Flu)ZrMe₂ is isopropylidene (cyclopentadienyl 1-fluorenyl)zirconium dimethyl and F15 is tris(pentafluorophenyl)boron.

A combination of aluminum alkyl and a Lewis acid was found to be necessary for reproducible, controllable, high efficiency polymerizations.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

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GROUP 1:

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EXAMPLE I

0.16 mmol of triethylaluminum (TEAI) Was dissolved in 5 ml of toluene and was added to a 2 liter Zipperclave reactor under 5 psig of nitrogen. Reactor temperature was set to 70 °C and one liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

30 35 mg of iPr(Cp-I-Flu)ZrMe₂ was dissolved in 10 ml of toluene. The catalyst was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 70 °C and the contents of the reactor were agitated for thirty minutes. At the end of the polymerization, the reactor was cooled and the unreacted propylene was vented from the reactor. There was no reaction product. The results are shown in Table I.

EXAMPLE II

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0.33 mmol of triethylaluminum (TEAI) was dissolved in 5 ml of toluene and added to a Zipperclave reactor. Reactor temperature was set to 70 °C and 1.0 liter of propylene was added to the reactor. The mixture was stirred for 15 minutes at 1200 rpm.

78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene to form a colorless solution. 60 45 mg of iPr(Cp-I-Flu)ZrMe₂ was dissolved in 10 cc of toluene to form a yellow solution. The two solutions were mixed together and formed a red solution which was mixed for 5 minutes at room temperature.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for thirty minutes. The reactor temperature increased to 90 °C. Unreacted propylene was vented from the reactor and the reaction product 50 was washed with acetone and dried in a vacuum.

The polymer was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

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EXAMPLE III

The procedure of Example II was repeated using 0.33 mmol of triethyl aluminum (TEAl), 27 mg of tris(pentafluorophenyl)boron and 20 mg of iPr(Cp-I-Flu)ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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EXAMPLE IV

10 The procedure of Example II was repeated using 0.16 mmol of triethyl aluminum (TEAl), 46 mg of tris(pentafluorophenyl)boron and 15 mg of iPr(Cp-I-Flu)ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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EXAMPLE V

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The procedure of Example II was repeated using 0.10 mmol of triethyl aluminum (TEAl), 46 mg of tris(pentafluorophenyl)boron and 35 mg of iPr(Cp-I-Flu)ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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EXAMPLE VI

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25 The procedure of Example II was repeated using 0.16 mmol of triethyl aluminum (TEAl), 46 mg of tris(pentafluorophenyl)boron and 35 mg of iPr(Cp-I-Flu)ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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EXAMPLE VII

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30 The procedure of Example II was repeated using 0.33 mmol of triethyl aluminum (TEAl), 46 mg of tris(pentafluorophenyl)boron and 35 mg of iPr(Cp-I-Flu)ZrMe₂. The contents of the reactor were agitated for thirty minutes. Unreacted propylene was vented from the reactor. There was no reaction product. The results are shown in Table I.

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EXAMPLE VIII

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45 The procedure of Example II was repeated using 0.16 mmol of trimethyl aluminum (TMA), 46 mg of tris(pentafluorophenyl)boron and 35 mg of iPr(Cp-I-Flu)ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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Group 2:

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EXAMPLE IX

0.16 mmol of triethyl aluminum (TEAl) was dissolved in 5 ml of toluene and was added to a 2 liter zipperclave reactor under 5 psig of nitrogen.

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Reactor temperature was set at 60°C and 1 liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

86 mg of MgCl₂ was slurried in 5 cc of toluene. 18 mg of iPr(Cp-I-Flu)ZrMe₂ was cannulated into the MgCl₂ slurry. The mixture was stirred for 12 hours to give a dark purple suspension.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for thirty minutes. Unreacted propylene was vented from the reactor and the reaction product was washed with a dilute HCl methanol solution and dried in a vacuum oven.

- 5 The polymer was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

10 Group 3:

EXAMPLE X

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One liter of propylene was added to the Zipperclave reactor. Reactor temperature was set to 70 C. 78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene. 58 mg of Et(Ind)₂ZrMe₂ was dissolved in 18 cc of toluene. The two solutions were mixed together for 5 minutes at room temperature.

- 20 The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The reactor temperature was maintained at 70 °C and the contents of the reactor were agitated for 35 minutes. Unreacted propylene was vented from reactor. There was no reaction product. The results are shown in Table I.

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EXAMPLE XI

- 30 0.33 mmol of triethylaluminum (TEAI) was dissolved in 5 ml of non coordinating solvent and added to a Zipperclave reactor. Reactor set point temperature was set to 70 °C and 1.0 liter of propylene was added to the reactor. The mixture was stirred for ten minutes at 1200 rpm.

78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene to form a colorless solution. 58 mg of Et(Ind)₂ZrMe₂ was dissolved in 10 cc of toluene to form a pale yellow solution. The two solutions were mixed together to form a clear dark yellow solution which was mixed for 5 minutes at room temperature.

- 35 The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The reactor temperature increased to over 95 °C and the contents of the reactor were agitated for six minutes. Unreacted propylene was vented from the reactor and the reaction product was washed with acetone and dried in a vacuum.

- 40 The polypropylene reaction product was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

EXAMPLE XII

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The procedure of Example XI was repeated using 0.66 mmol of TEAI, 27 mg of tris(pentafluorophenyl)-boron and 20 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 22 minutes. The results are shown in Table I.

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EXAMPLE XIII

- 55 The procedure of Example XI was repeated using 0.33 mmol of TEAI, 2.5 mg of tris(pentafluorophenyl)-boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

EXAMPLE XIV

The procedure of Example XI was repeated using 0.66 mmol of TEAI, 102 mg of tris-
 5 (pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30
 minutes. The results are shown in Table I.

EXAMPLE XV

10 The procedure of Example XI was repeated using 0.66 mmol of TEAI, 154 mg of tris-
 (pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30
 minutes. The results are shown in Table I.

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EXAMPLE XVI

20 The procedure of Example XI was repeated using 0.66 mmol of TEAI, 308 mg of tris-
 (pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30
 minutes. The results are shown in Table I.

25 Group 4:

EXAMPLE XVII

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The procedure of Example IX was repeated with 352 mg of magnesium chloride, 40 mg of Et(Ind)-
 ZrMe₂, 0.66 mmol of TEAI and a run time of thirty minutes. The results are shown in Table I.

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EXAMPLE XVIII

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The procedure of Example IX was repeated with 352 mg of magnesium chloride, 10 mg of Et(Ind)-
 ZrMe₂, 0.66 mmol of TEAI and a run time of thirty minutes. The results are shown in Table I.

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EXAMPLE XIX

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	Run #	Catalyst umol (mg)	Lewis Acid umol(mg)	Aluminum Alkyl mmol	Run Time min
5	1.	iPr(Flu)(Cp)ZrMe ₂ 89.8(35)	B(C ₆ F ₅) ₃ 0	TEA1 0.16	30
	2.	153(60)	153 (78.6)	0.33	30
	3.	51.2(20)	52.73(27)	0.33	30
	4.	38.4(15)	89.8(46)	0.16	30
10	5.	89.5(35)	89.8(46)	0.10	30
	6.	89.5(35)	89.8(46)	0.16	30
	7.	89.5(35)	89.8(46)	0.33	30
	8.			TMA 0.16	30
15	9.	89.5(35)	89.8(46)	MgCl ₂ TEAL	30
	10.	Et(Ind) ₂ ZrMe ₂ 45(18)	900(86)	B(C ₆ F ₅) ₃ 154(58)	0.66
	11.	154(58)	154(78.6)	0	35
	12.	53(20)	53(27)	0.33	6
20	13.	6.6(2.5)	6.6(2.5)	0.66	22
	14.	6.6(2.5)	200(102)	0.66	30
	15.	6.6(2.5)	300(154)	0.66	30
	16.	6.6(2.5)	600(308)	0.66	30
25	17.	Et(Ind)ZrMe ₂ 106(40)	MgCl ₂ 3700(352)	TEA1 0.66	30
	18.	27(10)	3700(352)	0.66	30
	19.	106(40)	1300(124)	0.66	30

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	Run #	Polymerization	Yield	Melting	Molecular	Molecular Weight
		Temp C		Temp C	Weight x 1000	Distribution
35	1.	70	0	-	-	-
	2.	70	123		57.6	1.9
	3.	70	7	110	64.3	2.0
	4.	70	58			
	5.	70	5	105	39	2.0
40	6.	70	168	105	61	1.9
	7.	70	110	123	55	2.0
	8.	70	167			
	9.	60	6	131	57	2.0
	10.	70	0	-	-	-
45	11.	70	117	113	15	4.2
	12.	70	70	122	17.5	3.5
	13.	70	0			
	14.	70	1	127	26	2.8
	15.	70	90	130	20	5.1
50	16.	70	33	129	25	3.7
	17.	70	49	133	31	1.9
	18.	70	47	130	29	2.4
	19.	70	8	130	30	2.0

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For the F15 catalyst system, higher efficiencies were obtained by increasing the B:Zr molar ratio significantly above 1:1. This implies that the lower efficiencies are partly due to incomplete ionization by F15.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings.

It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

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Claims

1. A catalyst system comprising:
- 10 a) a neutral metallocene compound;
- b) an aluminum alkyl; and
- c) a Lewis acid;
- wherein the aluminum alkyl is of the general formula AlR_3 where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl,
- 15 wherein the neutral metallocene compound is of the general formula:
 Cp_2MR_p
 wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4.
- 20 wherein the Lewis acid is of sufficient acidity to ionize a neutral metallocene compound to form a cationic metallocene catalyst, and
 wherein the ligands of the Lewis acid are not reactive with the metallocene cation.
- 25 2. A catalyst as recited in Claim 1 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
- 30 3. A catalyst as recited in Claim 2 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.
4. A catalyst as recited in Claim 1 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
5. A catalyst as recited in Claim 4 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylenebis(indenyl)zirconium dimethyl and isopropylidene(cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
6. A catalyst as recited in Claim 1 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.
7. A catalyst as recited in Claim 6 wherein the aluminum alkyl is triethylaluminum.
- 35 8. A catalyst as recited in Claim 1 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.
9. A catalyst as recited in Claim 8 wherein the Lewis acid is tris(pentafluorophenyl)boron.
10. A process for preparing a catalyst comprising:
- a) mixing a Lewis acid with a neutral metallocene compound; and
- 40 b) allowing contact between the ionizing ionic compound and the neutral metallocene compound;
 wherein the neutral derivative of a metallocene is of the general formula:
 Cp_2MR_p
 wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4;
- 45 11. A process as recited in Claim 10 wherein the olefin is propylene.
12. A process as recited in Claim 10 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
13. A process as recited in Claim 10 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
- 50 14. A process as recited in Claim 13 wherein the M is zirconium.
15. A process as recited in Claim 14 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylenebis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
- 55 16. A process as recited in Claim 10 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.
17. A catalyst as recited in Claim 16 wherein the Lewis acid is tris(pentafluorophenyl)boron.
18. A process for polymerization of olefins comprising:

- a) mixing an aluminum alkyl with an olefin;
 - b) mixing a neutral metallocene compound with a Lewis acid;
 - c) mixing the metallocene-Lewis acid mixture with the aluminum alkyl-olefin mixture.
- 5 wherein the aluminum alkyl is of the general formula AlR_3 where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl; and
- wherein the neutral metallocene compound is of the general formula:
 CP_2MR_p
wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4.
- 10 19. A process as recited in Claim 18 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.
- 20 20. A process as recited in Claim 19 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl ranges from 0.01:1:0.1 to 5:1:350.
21. A process as recited in Claim 20 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl ranges from 0.5:1:05 to 4:1:25.
22. A process as recited in Claim 21 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl is 0.02:1:1.
23. A process as recited in Claim 21 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl is 0.01:1:1.
24. A process as recited in Claim 16 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.
22. A process as recited in Claim 21 wherein the aluminum alkyl is triethylaluminum.
23. A catalyst as recited in Claim 18 wherein the Lewis acid is chosen from the group consisting of all 25 Lewis acids containing boron and magnesium chloride.
24. A catalyst as recited in Claim 23 wherein the Lewis acid is tris(pentafluorophenyl)boron.

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